COAL-LIKE SUBSTANCES FROM LOW-TEMPERATURE PYROLYSIS AT VERY LONG REACTION TIMES

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ABSTRACT

The importance of long reaction times in the coalification process has been demonstrated in the laboratory. Samples of cellulose and pine sawdust in evacuated, sealed glass vials have been heated at 200° C for two years. Black coal-like chars were produced; heating at 200° C for hours produced very little chemical change. The chars were characterized by infrared and electron spin resonance spectra. The infrared spectra of the pine sawdust char and of a subbituminous coal are nearly identical, except for differing carbonyl absorption. The spectrum of the cellulose char is also similar to that of the subbituminous coal. The electron spin resonance results show that g values and line widths are nearly identical for the chars and are very close to similar values for subbituminous coal.

200° C is considered a reasonable coalification temperature; depth of burial can provide such temperatures. The experimental coalification obtained in only two years appears to substantiate the hypothesis that geologic time could produce all ranks of coals at temperatures below 200° C.

INTRODUCTION

In the study of the structure and properties of coal, attempts have been made to prepare synthetic coals, principally by pyrolysis methods. Chars having properties identical to those of coals have not been produced. Initial attempts at studying the infrared spectra of coal-like chars prepared by pyrolysis of pure materials were carried out several years ago.[1,2] The pyrolysis method used was that of Smith and Howard, who had prepared from cellulose, chars that had some of the properties of coals.[3] We studied the infrared spectra of chars prepared from cellulose over a range of temperatures; the spectrum of a 400° C cotton char somewhat resembled that of high-volatile bituminous coal.[1,2] The spectrum of this char showed a definite carbonyl absorption band which is not present, except as a weak shoulder, in infrared spectra of coals. Carbohydrate chars prepared at 300°, 400°, and 500° C produced absorption bands in the aromatic region that were identical to the aromatic bands produced respectively by lignite, high-volatile bituminous, and anthracite coals; less similarity was observed in other parts of the spectra.[4] Similarities of reaction of coal and the carbohydrate, sucrose, were nicely illustrated by the identical spectra of products obtained in hydrogenation studies.[5]

Friedman and coworkers studied many coal-like chars prepared by pyrolysis of pure oxygenated compounds, mostly at 400° C and reaction times of one hour; several properties of these chars, including infrared spectra, have some resemblance to the corresponding properties of coals.[6] Pure hydrocarbons have been charred in the presence and absence of molecular oxygen; only when oxygen was present did the infrared spectra of the chars resemble those of coals, particularly in the 1600 cm^{-1} region.[4,7] Unless oxygen is involved the 1600 cm^{-1} band is weak or non-existent; thus it is believed that the strong 1600 cm^{-1} band involves carbonyl groups.[4,7]

In another study, chars were prepared from O^{18}-labelled compounds in an attempt to ascertain whether an isotopic shift would occur at 1600 cm^{-1} and would thus indicate that carbonyl groups are involved. No isotopic shift was obtained; the infrared spectrum of an O^{18}-labelled chelate, dibenzoylmethane, demonstrated that if a C=O group is very strongly chelated the C=O vibration becomes completely delocalized and no isotopic shift occurs.[8,9]

In attempting to simulate coal the following principal variables are available: Starting material, temperature, rate of heating, reaction time, and pressure. The effect of pressure is considered minor compared to the effect of temperature.[10,11] The effect of pressure during many eons may be important; temperature during many eons is certainly important. Though presumptious, it was assumed that some slight indication of the effect of geologic time might be observable in the laboratory. Pyrolysis experiments involving reaction times of years, rather than hours or days, were decided on. Temperatures at or below 200° C were chosen. The spectral methods selected for investigation of the coal-like properties of the chars were infrared and electron spin resonance spectrometry.

EXPERIMENTAL PROCEDURE

Pyrolyses. Pyrolytic oxidation of cotton and pine-wood sawdust was carried out at low temperatures. Two sets of samples were heated in air at 150° C and at 200° C for 10 months; the chars produced were investigated by infrared spectrometry.

For the pyrolysis experiments without air, samples of cotton, 0.43 g, and pine-wood sawdust, 0.20 g, were placed in heavy-walled Pyrex tubes which were evacuated and sealed. The sample-tube volumes were 3.1 cc. The samples were heated at 200° C for two years. Gases and other volatile products were analyzed by mass spectrometer.

Instrumental investigation. The principal methods of characterizing the pyrolysis products were infrared (Perkin-Elmer Model 521)[a] and electron paramagnetic resonance spectrometry (Varian Associates Model V-4500). Preliminary examinations of the chars were also made on a high-resolution mass spectrometer (Consolidated 21-110B). Ultimate microanalyses of the chars will be performed by the Huffman Laboratories; analyses will destroy the small samples remaining so none will be carried out until all possible experimental investigations are concluded.

RESULTS AND DISCUSSION OF RESULTS

Low pyrolysis temperatures and reaction times of several months were decided on in an attempt to simulate mild coalification conditions. Temperatures in the 200° C range are considered realistic; many coals have been subjected to such temperatures due to depth of burial. Initially pyrolytic oxidation runs were made on cellulose and on pine sawdust at 150° C in the presence of air. Pyrolysis of these materials for 10 months gave black insoluble solids having infrared spectra which indicated extensive oxidation. The second set of investigations was carried out at 200° C in the presence of air; as expected greater pyrolytic oxidation was produced. Then pyrolysis runs in the absence of air were initiated with samples of cotton and of pine sawdust sealed in evacuated, heavy-wall glass tubes. The samples were heated at 200° C for two years. Tarry products were observed during the early stages of pyrolysis; these became solid char long before two years elapsed. The gas produced in the pyrolysis of the cotton sample was lost by an explosion; most of the char was salvaged. The vial containing the pine sawdust

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[a] Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

char was then opened, with release of considerable pressure of gas (6.3 atm). A thin film of colorless liquid, mostly water, vaporized completely into the evacuated gas-handling system. The gas analysis in table 1 shows mainly H_2O and CO_2. Both chars were completely black; the yield of char from pine sawdust was about 85 percent. The infrared spectra of both samples are shown in figure 1, along with a spectrum of a subbituminous coal (Dietz bed, Wyoming, 70.8 percent C, m.a.f. Ultimate analysis is given in table 2). The spectra of the coal and the sawdust char are remarkably similar. In addition to the more obvious spectral similarities at 3400, 2950, 2920, 2860, 1600, 1440, 1370, 1280, and 1180 cm^{-1}, there is a considerable similarity at the aromatic band positions, 860, 810, and 750 cm^{-1}. The aromatic bands are weak in the spectra of subbituminous coals, but the similarity of the coal and char absorption patterns in this region is impressive. It is apparent from these spectra that it is possible over a long period of time to approach a coal-like spectrum, even at a low temperature.

Table 1.- Mass spectrometric analysis of gases from 200° pyrolysis of pine sawdust. Volume of vial, 3.1 cc; pressure in vial 6.3 atm.

	Mole percent	Milligrams
Carbon dioxide	25.8	9.7
Water	57.9	8.9
Methanol	3.9	1.1
Dimethyl ether	12.4	4.9
	100.	
Total carbonyl compounds (estimate)		5.
		29.6

Table 2.- Ultimate analysis of Dietz bed subbituminous coal, Big Horn Mine, Wyoming

	Weight percent, m.a.f.[a/]
C	70.83
H	5.06
N	1.02
S	0.59
O (by difference)	22.50

a/ Ash content 3.23 percent (moisture-free)

Heating from room temperature to 190° C in one hour, the cellulose of Smith and Howard had produced a brown char (yield, 89 percent) but the infrared spectrum, as well as the elemental analysis, resembled those of cellulose with only minor differences.[4/] No coal-like spectral features were observed. In the spectrum of the sawdust char there is a 1700 band as we have seen before in char spectra. But, for the first time in spectra of chars prepared at low temperature the 1600 band is more intense than the 1700 and thus is approaching the situation in coal spectra. Thus the very long heating time has produced a definite decrease in carbonyl-containing structures. In the coalification process it is feasible that simple

carbonyl groups are first formed in the early stages of pyrolysis and then are slowly converted to some other structure(s) during geologic time. Possibly the carbonyl groups are converted to modified carbonyl structures which can produce the intense 1600 cm^{-1} absorption band observed in infrared spectra of coals and chars. Substantiation of this hypothesis may exist in the behavior of carbonyl groups in chars that were prepared from cellulose at 300°, 400°, and 500° C.[4,7] In the spectrum of the 300° char the carbonyl absorption is stronger than the unknown absorption at 1600 cm^{-1}. Relative intensities are given in table 3. For the 400° C char the intensities become more similar; the spectrum of the 500° C char shows reversal of intensities with complete disappearance of the simple carbonyl absorption band.[4,7] These changes may be explainable by the postulation of conversion into a modified carbonyl-containing structure. This structure could be the conjugated chelated structure, such as the enol form of acetylacetone, that has been proposed previously as the source of the 1600 cm^{-1} absorption band.[2,14] It is interesting that the same kind of change, though more subtle, occurs in coals; infrared spectra of lignites and low rank coals have weak absorption shoulders at 1700 cm^{-1} which gradually disappear from spectra of higher rank coals.[15,16] For the coals the conversion of carbonyl compounds to the presumed conjugated chelated carbonyls is farther advanced than it is in these chars which were prepared at reaction times of only one hour.[4,7]

Table 3.- Relative absorption intensities in the infrared spectra of 300°, 400°, and 500° C cellulose chars at 1700 cm^{-1} (carbonyl compounds) and 1600 cm^{-1} (presumably chelated conjugated carbonyl groups)

Cellulose char, preparation temperature	Relative intensities, percent	
	1700 cm^{-1}	1600 cm^{-1}
300° C	78	22
400° C	59	41
500° C	0	100

Electron spin resonance spectrometry has been applied to the study of chars of cotton and pine sawdust. Values for the parameters are given in table 4 along with comparative values for subbituminous coal.[17] As with the infrared, the results for the chars are closely similar to those for the coal vitrain. The fact that a signal is detected is of interest for it demonstrates that stable free radicals can be formed in natural materials on exposure to very mild heating conditions. There are not many examples of free radical signals obtained from chars produced at temperatures as low as 200° C. It is probable that even lower temperatures will produce free radicals in carbonaceous materials over long periods of time.

Table 4.- Electron spin resonance data for chars and subbituminous coal vitrain

	Cotton char	Pine sawdust char	Subbituminous vitrain, Wyoming
g-Value	2.00321 ± 0.0001	2.00314 ± 0.0001	2.00381 ± 0.0001
Line width, gauss	5.6 ± 0.5	6.3 ± 0.5	8.0 ± 0.5

Preliminary work on mass spectra of these chars has shown mononuclear and polynuclear aromatics similar to those found in mass spectra obtained on coal; this investigation is continuing.

The striking importance of time in pyrolysis reactions has been demonstrated. If chars as coal-like as these can be produced in two years, at temperatures that have little effect during short times, then it appears that in geologic times coal could be produced at temperatures much lower than 200° as proposed by various people.[10,12,13] Our next experiments will run for greater lengths of time, with the expectation of producing chars that will resemble higher ranks of coal. Under the same experimental conditions that produced chars similar to subbituminous coal, chars having the characteristics of bituminous coals possibly could result from heating at 200° C for three or four years. It is expected that the distinctive aromatic absorption bands in the infrared spectra and the electron spin resonance parameters, of bituminous coals will be duplicated in such chars.

On the question of whether cellulose or lignin is the more important precursor of coal the results herein described indicate that at low temperatures and long reaction times the coal-like chars obtained from cellulose and from lignin plus cellulose are very similar. It may be significant that greater similarity between coal and char infrared spectra is observed for the char from lignin plus cellulose (pine sawdust).

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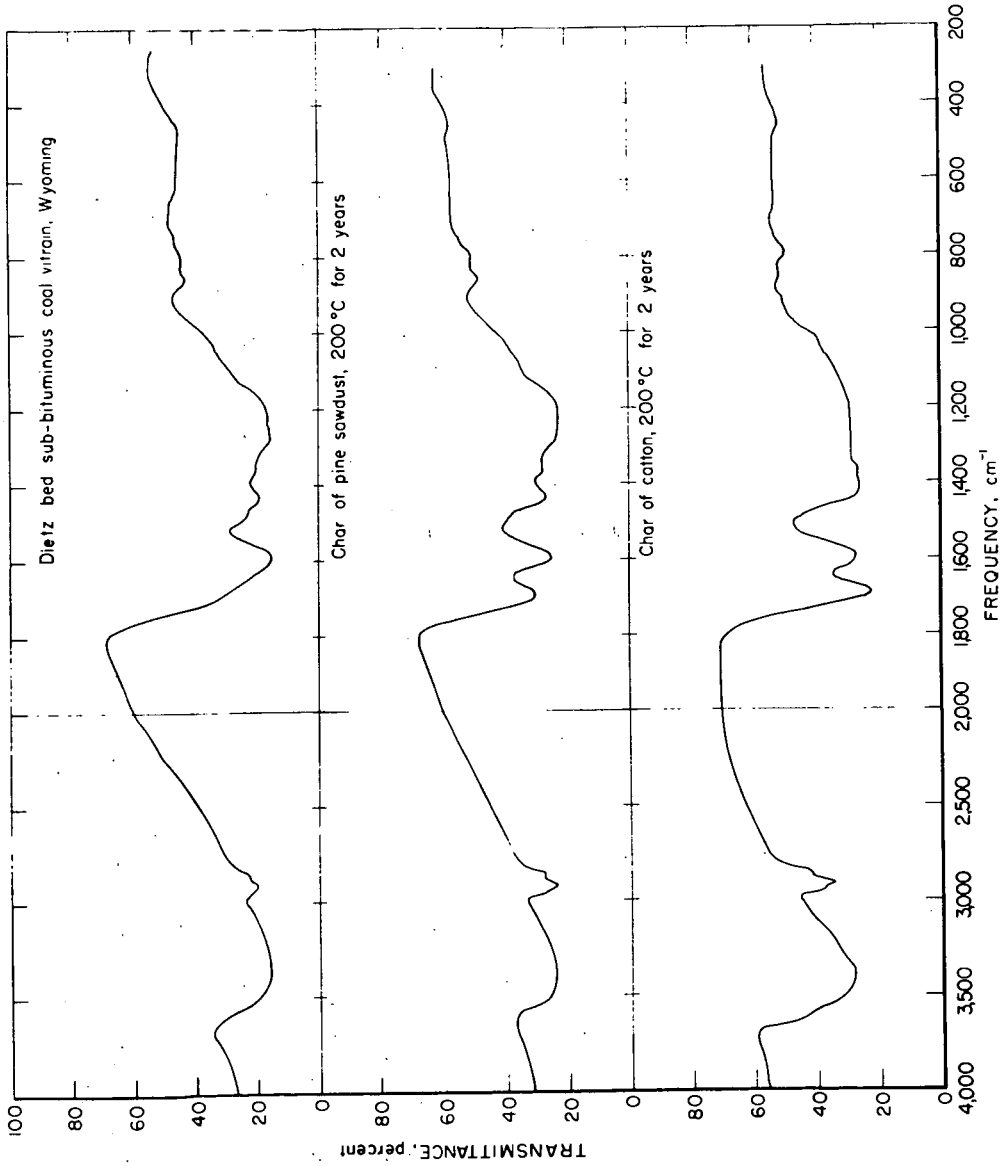

Figure 1.- Infrared spectra of Dietz bed subbituminous coal vitrain, 200° char of pine sawdust, and 200° char of cotton.